

Spectroscopic Assessment of the Nickel Species in Contaminated Soils Using A Linear Combination Analysis Approach

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Results and Discussion

Fig 1a-c. *In situ* μ -XRF elemental mapping of the Ni contaminated soils along with the scatter plots showing the poor correlation of Ni with Fe and Mn components of the soil. Ni species appear as discrete spherical aggregated particles with size distribution ranging up to a maximum of 50 μ m in diameter.

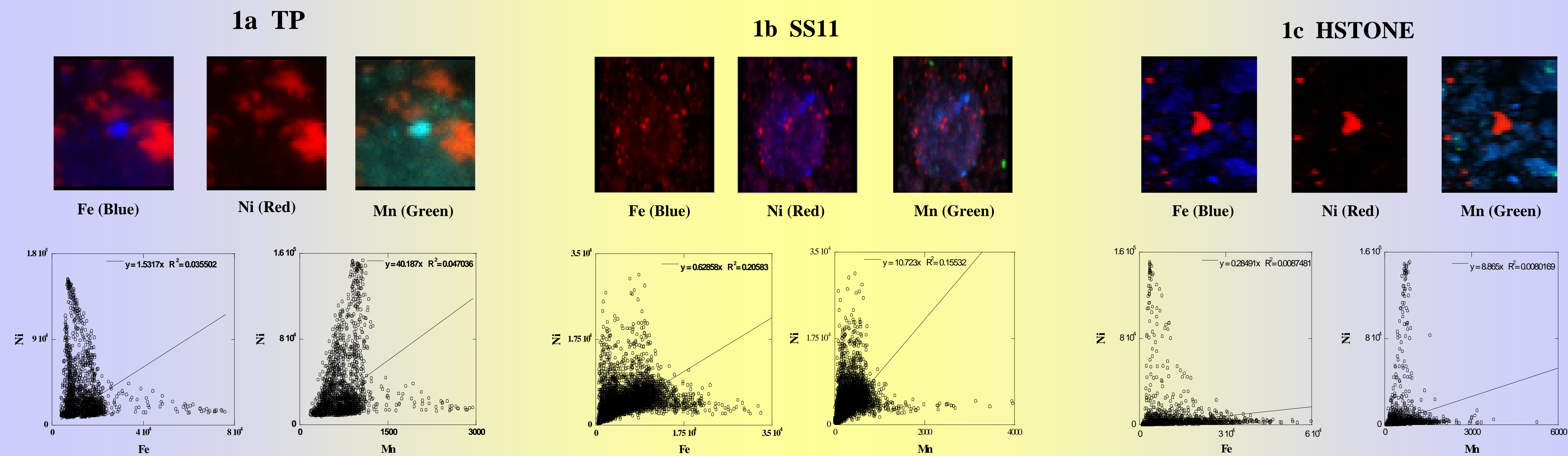


Fig. 4. Fourier transforms of the Ni K-edge fluorescence XAS spectra of contaminated soils filtered over 2.5-9.2 \AA^{-1} and fitted with the NiO model over 0.6-3.6 \AA^{-1} . Solid lines are the experimental data and dashed lines are the fits.

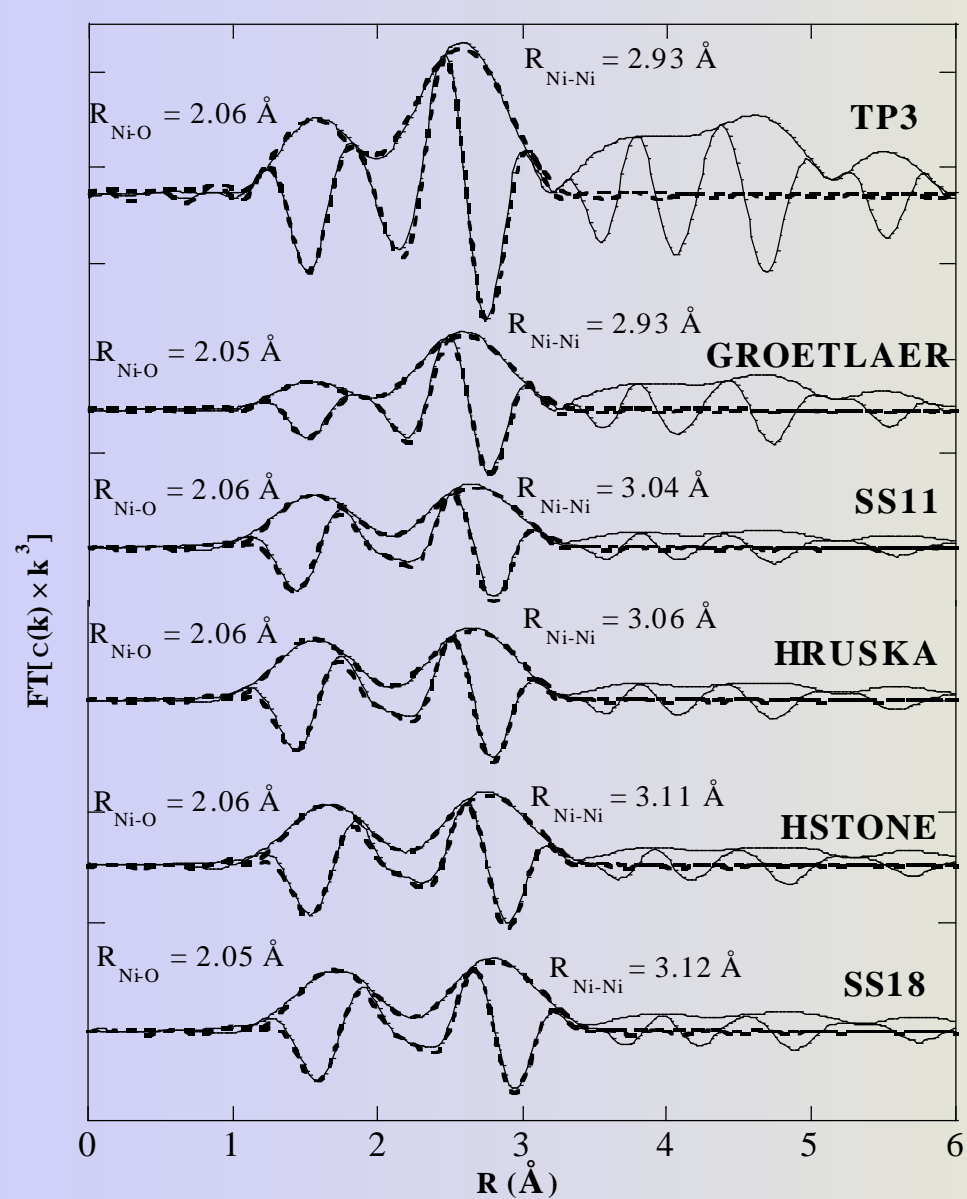
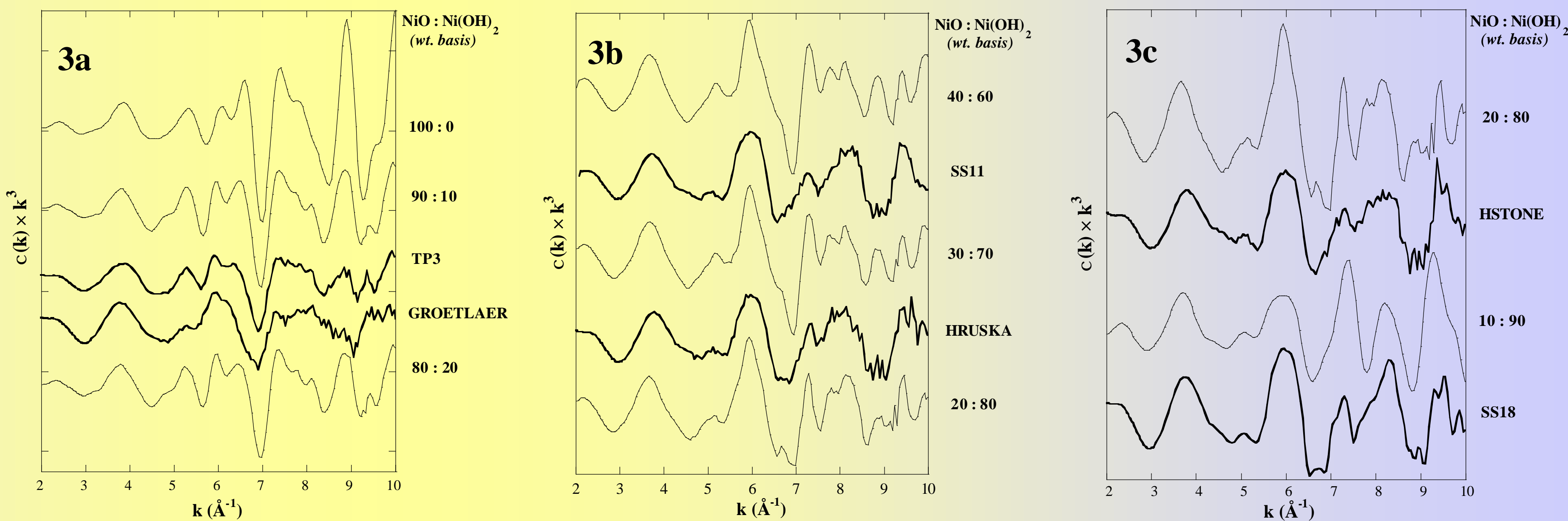


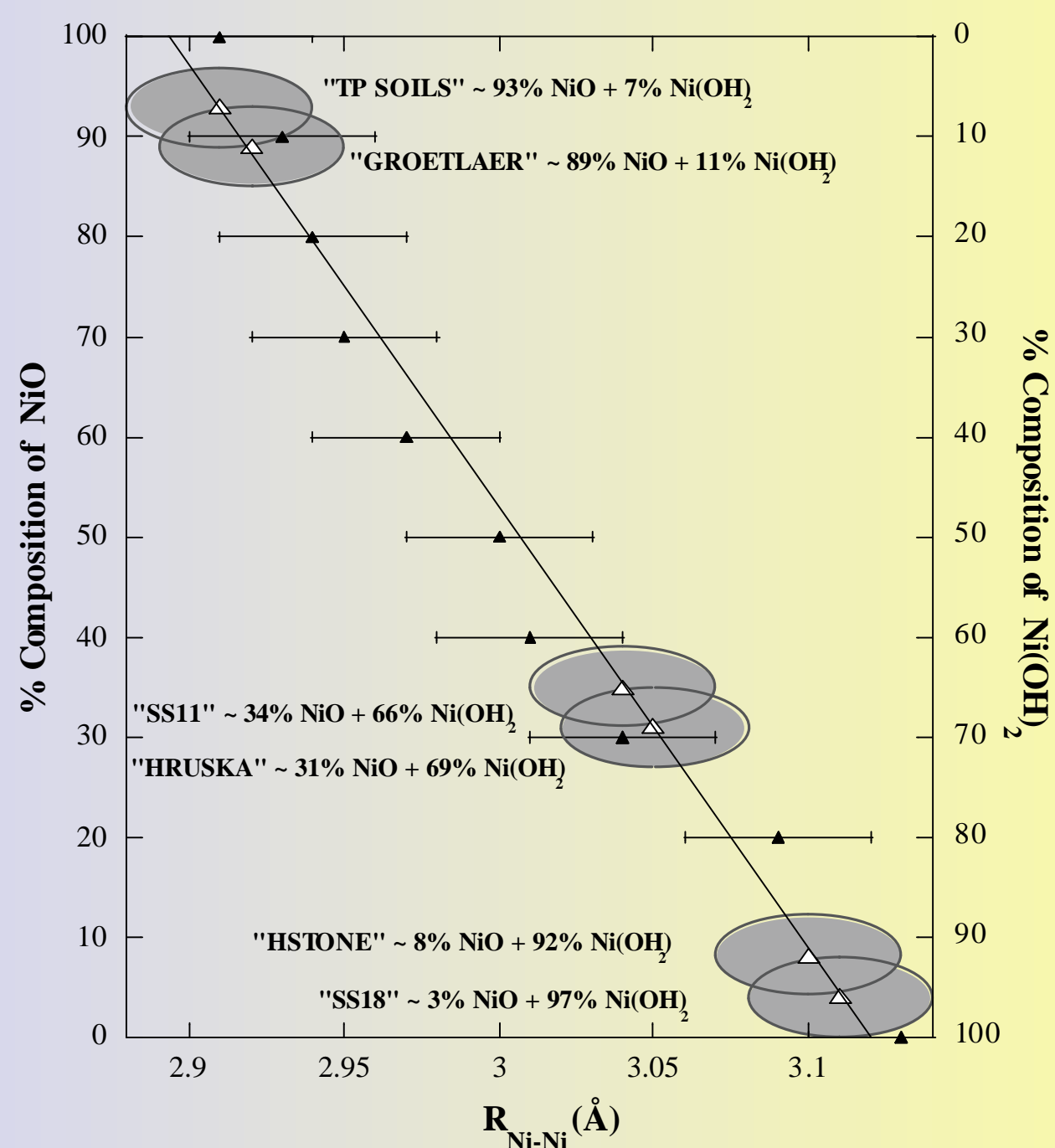
Fig.3a-c. Lack of evidence for Ni associations with Al, Fe or Mn suggests that Ni exists predominantly as oxide or hydroxide species. Hence, the normalized, k^3 -weighted, and averaged Ni K-edge fluorescence bulk XAS spectra of Ni contaminated soils are compared with transmission XAS spectra of NiO + Ni(OH)₂ mixtures



Conclusions

Fig. 5 Linear Combination Approach

Both the bulk XAS analyses and the micro-XAS analyses confirmed that Ni predominantly exists as oxide or hydroxide species. As a result the linear combination analyses on these soil samples was constrained to estimating the contributions of NiO and Ni(OH)₂. For this purpose, mixtures of NiO and Ni(OH)₂ were studied in transmission mode. The average radial distances of the second shell ($R_{\text{Ni-Ni}}$) systematically increased with an increase in the percent fraction of Ni(OH)₂ from 2.92 \AA for 100% NiO to 3.11 \AA for 100% Ni(OH)₂. Thus $R_{\text{Ni-Ni}}$ is a linear function of the percent fraction of NiO or Ni(OH)₂. This linear combination model provides an estimate for the composition of Ni species present in the contaminated soils within an error of $\pm 10\%$.



Summary of Findings

- In the soils located closer to the smelter (pH 5.9-6.6), approximately 90-95% of the Ni species present exists as NiO.
- In the soil samples collected from the intermediate locations (pH 6.5), contained approximately 30-35% NiO and the remaining Ni was identified as disordered hydroxide.
- In the soils located at least 3 km away (pH > 7.0), nearly 92-97% of the Ni species exist as disordered hydroxide.
- Ni is poorly associated with Al, Fe, or Mn components of the soils.
- CAUTION!** These associations must not be completely ruled out since it is likely that the signals from the high concentrations of NiO species may swamp the signals arising from the sorption complexes.
- To obtain any quantitative inferences on the physicochemical processes governing the mobility and bioavailability of nickel in these soils, further fundamental studies are needed.

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